

Thermodynamic consistency and fast dynamics in phase field crystal modeling

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A general formulation is presented to derive the equation of motion and to demonstrate thermodynamic consistency for several classes of phase field models at once. It applies to models with a conserved phase field, describing either uniform or periodic stable states, and containing slow as well as fast thermodynamic variables. The approach is based on an entropy functional formalism previously developed in the context of phase field models for uniform states [P. Galenko and D. Jou, Phys. Rev. E **71**, 046125 (2005)] and thus allows to extend several properties of the latter to phase field models for periodic states (phase field crystal models). In particular, it allows to demonstrate the concept of thermodynamic consistency for phase field crystal models with fast dynamics.

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Phase field modeling has become a versatile tool for studying the dynamics of systems out of equilibrium, and has found numerous applications in materials science [1, 2, 3, 4]. For instance, consider a material that is disordered at high temperature and has two stable phases at low temperature. Upon quenching the material from high to low temperature, grains with the different stable phases will develop, grow and compete with each other. Phase field modeling is able to describe the time evolution of such a process. In a phase field model for this example, a continuous function of space and time $\psi(\mathbf{x}, t)$ is introduced – the phase field variable – that assumes a different constant value for both stable phases. Near an interface between two grains, the value of ψ rapidly changes. The phase field variable in this example can be interpreted as an order parameter to represent the relative mass fraction of both phases. A major advantage of phase field modeling is that the phase field contains information on the location of all interfaces in the system, without the need for explicit interface tracking. Another advantage is that it focusses on gross features that are common to many systems. System-specific details are incorporated by the interpretation given to the phase field variable, and by the values given to the phenomenological parameters in the model equations. Systems that are similar according to appropriate criteria, are therefore described by the same phase field model. Several important classes of such models are ordered in Tab. I. The major goal of this paper will be to present a unified description of four of these classes.

$$F_1[\psi] = \int_V \left[\frac{\epsilon^2}{2} |\vec{\nabla} \psi|^2 + f(\psi) \right] dV, \quad (1)$$

$$F_2[\psi] = \int_V \left[\frac{\epsilon_1^2}{2} |\vec{\nabla}^2 \psi|^2 - \frac{\epsilon_2^2}{2} |\vec{\nabla} \psi|^2 + f(\psi) \right] dV, \quad (2)$$

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta F_i}{\delta \psi}, \quad (3)$$

		uniform	uniform	periodic	periodic
		cons.	non-cons.	cons.	non-cons.
slow only	free energy	Eq. 1	Eq. 1	Eq. 2	Eq. 2
slow only	eq. motion	Eq. 3	Eq. 4	Eq. 3	Eq. 4
slow only	model	CH	AC	PFC	SH
slow+fast	eq. motion	Eq. 25 in Ref. 22	Eq. 26 in Ref. 22	Eq. 3 in Ref. 18	<i>yet to be developed</i>
slow+fast	model	MCH	MAC	MPFC	MSH

TABLE I: A classification of eight different phase field models according to the nature of the equilibrium state they describe (uniform or periodic) and the properties of the phase field variable (conserved or non-conserved). Models that describe slow dynamics only are distinguished from models that include fast dynamics as well. For each model, the name of the model and the equation of motion is given, as well as the free energy (where appropriate). The acronyms refer to Cahn-Hilliard (CH), Allen-Cahn (AC), Phase-Field Crystal (PFC) and Swift-Hohenberg (SH) – see text. The M in the last line stands for ‘Modified’ throughout. This paper presents a unified description for the models that are printed in underlined bold face, and demonstrates thermodynamic consistency for all four of them.

$$\frac{\partial \psi}{\partial t} = - \frac{\delta F_i}{\delta \psi}. \quad (4)$$

One gross system property to distinguish different classes, is whether its stable states are spatially *uniform* or *periodic* (Tab. I). If we neglect details at the atomic scale, the two stable states of our illustrative quenched alloy can be considered as being spatially uniform. On the other hand, Rayleigh-Bénard convection in a thin fluid layer between two plates leads to periodic stable states with regular patterns of convection cells [15]. A free energy functional $F_i[\psi]$ is postulated for the uniform and periodic cases, respectively (Eqs. 1 and 2). From this free energy functional, an equation of motion for the system can be obtained by Eqs. 3 or 4. Eq. 3 applies when the

integral of the phase field variable over space is time independent, in which case the phase field is called *conserved* (Tab. I). In the other case, Eq. 4 applies and the phase field is *non-conserved*. The distinction between conserved and non-conserved order parameters is another criterion to distinguish different classes. The fact whether the equations of motion properly describe the system under consideration or not, is an *a posteriori* justification of the postulate for the free energy functional.

Eq. (1) was originally introduced by Landau, and since then became the fundamental functional to derive phase field (PF) models. The potential $f(\psi)$ has a double-well structure corresponding to the two stable phases described by the order parameter ψ . The squared gradient term $|\vec{\nabla}\psi|^2$ accounts for fluctuations in the order parameter and ϵ is a phenomenological parameter that needs to be tuned for every particular system. Systems with uniform stable states and a conserved order parameter were studied half a century ago [5], and their equation of motion is now called the Cahn-Hilliard equation. The quenched alloy mentioned before is an example of this. Uniform equilibrium states with a non-conserved order parameter are described by the Allen-Cahn equation [6]. Further examples have been given in the context of polymer mixtures [7], alloys [8, 9], liquid-crystals [10, 11], and in cosmology [12].

For systems with stable states that are not spatially uniform, the Landau form of the free energy functional Eq. (1) is not valid any more. The appropriate energy functional, written in a general form [14], is now Eq. 2. The symbols have the same meaning as for Eq. 1, only there are now two phenomenological parameters ϵ_1 and ϵ_2 . The Swift-Hohenberg equation [15] describes systems where the stable states are periodic and the order parameter is non-conserved. For the case of periodic systems with a conserved order parameter, an equation of motion has only recently been derived: the Phase Field Crystal (PFC) model [13, 14]. It is a simple version of more elaborate density functional theories of liquid/crystal interfaces [16, 17]. This model captures features at the atomic scale, and thus contains highly detailed physical information about the system's structure. Such models can describe many of the basic properties of polycrystalline materials that are realized during non-equilibrium processing.

An important concept in phase field modeling is *thermodynamic consistency*. This means that in the limit of infinitely sharp interfaces between the different phases, the phase field equation of motion reduces to the phenomenological sharp interface equations that are adopted in a variety of analytical and numerical studies of moving boundary problems. Demonstrating thermodynamic consistency for a class of systems places the usage of a phase field for this class upon a solid theoretical foundation [3]. Once thermodynamic consistency has been proven, a phase field model can be formulated for a prob-

lem, for which sharp interface models are not yet available. Bi and Sekerka [19] showed thermodynamic consistency for CH and AC systems. Simultaneously, they derived the equation of motion for such systems from an *entropy* functional. This is an alternative to applying Eqs. 3 or 4 to the free energy functionals 1 or 2, and this alternative has the advantage of being more generally applicable.

So far, our discussion involved only systems with *local equilibrium*, where the movement of interfaces is ‘slow’, and classic irreversible thermodynamics applies. The movement of interfaces can be much faster in processes as e.g. rapid solidification [20, 21], where the system can be far away from local thermodynamic equilibrium. Galenko and Jou [22] have shown how extended irreversible thermodynamics can be used to develop a thermodynamically consistent phase field model that can deal with such fast dynamics using the entropy functional formulation (MCH and MAC models in Tab. I). Fast dynamics could be included by using an *extended* space of independent variables formed by the union of the classical ‘slow’ phase field variables, whose behavior is governed by conservation laws, or an evolution of the phase field, and the additional space of ‘fast’ non-conserved thermodynamic variables, which consists of nonconserved variables with a relatively high rate of decay, for example, the flux of a conserved phase field variable, or the time derivative of a non-conserved phase field variable [22].

For systems with periodic stable states, Stefanovic *et al.* [18] were recently able to formulate an equation of motion that does not only describe time evolution at the ‘slow’ diffusive time scale – which is what the PFC equation of motion does – but also time evolution at the much faster time scale of elastic interactions. They called this the Modified Phase Field Crystal (MPFC) model, and demonstrated it provides physically meaningful results for nanocrystalline solids with high strain rates. However, its equation of motion was postulated, and not obtained formally from a free energy or entropy functional.

We will present now a single derivation that leads to the equations of motion for CH, MCH, PFC and MPFC models (see Tab. I) as special cases. Simultaneously, thermodynamic consistency will be proven for all four models. It is inspired both by the entropy functional formulation of Bi and Sekerka [19] and the extended set of slow and fast thermodynamical variables by Galenko and Jou [22]. One distinction from previous unification attempts is that our approach does not require *ad hoc* assumptions of including the squared gradient and the squared Laplacian terms in the free energy functional [1, 2, 13, 14] or in the entropy functional [19, 22].

The derivation applies the extended space of independent variables \mathbf{E} . We restrict our analysis to a conserved phase field variable ψ and use the following *extended*

space of independent variables \mathbf{E} :

$$\mathbf{E} = \{C\} \cup \{F\} = \{\psi\} \cup \{\vec{j}_\psi, \vec{\nabla}\psi, \nabla^2\psi\}, \quad (5)$$

Where $\{C\}$ is the classical ‘slow’ phase field variables, and $\{F\}$ is the extended space of ‘fast’ non-conserved thermodynamic variables. The flux \vec{j}_ψ was introduced in Ref. 22, and the *two new extended* independent variables $\vec{\nabla}\psi$ and $\nabla^2\psi$ in Eq. (5) are, to our knowledge, introduced here for the first time. With these two extended independent variables, it becomes a natural result to include the squared gradient term $|\vec{\nabla}\psi|^2$ and the squared Laplacian term $(\nabla^2\psi)^2$ in the entropy functional, and obtain all four equations in a unified model.

For the local nonequilibrium system described above, we postulate the existence of a local generalized entropy density s whose set of variables is the extended space \mathbf{E} of Eq. (5). The generalized Gibbs equation for s is described by

$$s(\psi, \vec{j}_\psi, \vec{\nabla}\psi, \nabla^2\psi) = s_e(\psi) + s_{ne}(\vec{j}_\psi, \vec{\nabla}\psi, \nabla^2\psi), \quad (6)$$

where s_e is a local equilibrium contribution defined on the set $\{C\}$ of the classic ‘slow’ variables, and s_{ne} is a nonequilibrium part of the generalized entropy defined on the space $\{F\}$ of the independent ‘fast’ variables, and can be written in the form

$$s_{ne} = -\frac{\alpha_1}{2}|\vec{j}_\psi|^2 - \frac{\alpha_2}{2}|\vec{\nabla}\psi|^2 - \frac{\alpha_3}{2}(\nabla^2\psi)^2. \quad (7)$$

α_1 , α_2 and α_3 are system-specific parameters, and could be either positive or negative. The first term $-\alpha_1|\vec{j}_\psi|^2/2$ is from Ref. 22. It has the physical meaning of a diffusion constant, and thus can be determined quantitatively. The second term $-\alpha_2|\vec{\nabla}\psi|^2/2$ and third term $-\alpha_3(\nabla^2\psi)^2/2$ are obtained by symmetry arguments: since we treat all the additional extended variables \vec{j}_ψ , $\vec{\nabla}\psi$, $\nabla^2\psi$ on equal footing, there is no reason not to write all the terms in a similar way. The physical interpretation of the parameters α_2 and α_3 was discussed in Ref. 14, and we will come back to this point later in the paper.

For the system described by the extended set \mathbf{E} of variables, Eq. (5), the local balance law for the phase field variable ψ is given by

$$\frac{\partial\psi}{\partial t} = -\nabla \cdot \vec{j}_\psi, \quad (8)$$

and the evolution of entropy density is defined by

$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{j}_S + \sigma_S, \quad (9)$$

where σ_S is the non-negative local entropy production. The entropy functional takes the following form:

$$S = \int_V s(\psi, \vec{j}_\psi, \vec{\nabla}\psi, \nabla^2\psi) dV. \quad (10)$$

According to Eq. (9), the change of the total entropy S in time t is described by

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{ex} + \left(\frac{dS}{dt}\right)_{in}, \quad (11)$$

where

$$\left(\frac{dS}{dt}\right)_{ex} = - \int_V \vec{\nabla} \cdot \vec{j}_S dV = - \int_A \vec{j}_S \cdot \hat{n} dA \quad (12)$$

is the external exchange of entropy due to entropy flux \vec{j}_S and

$$\left(\frac{dS}{dt}\right)_{in} = \int_V \sigma_S dV \quad (13)$$

is the internal production of entropy due to dissipation within the system. In Eqs. (12) and (13), A is the outer surface of sub-volume V and \hat{n} is the normal vector to the surface. On the other hand,

$$\begin{aligned} \frac{dS}{dt} &= \int_V \left[\frac{\partial s}{\partial \psi} \dot{\psi} + \frac{\partial s}{\partial \vec{j}_\psi} \cdot \dot{\vec{j}}_\psi + \frac{\partial s}{\partial (\vec{\nabla}\psi)} \cdot \dot{\vec{\nabla}}\psi + \frac{\partial s}{\partial (\nabla^2\psi)} \nabla^2 \dot{\psi} \right] dV \\ &= \int_V \left[\frac{\partial s}{\partial \psi} \dot{\psi} - \alpha_1 \vec{j}_\psi \cdot \dot{\vec{j}}_\psi - \alpha_2 \vec{\nabla}\psi \cdot \dot{\vec{\nabla}}\psi - \alpha_3 \nabla^2\psi \nabla^2 \dot{\psi} \right] dV. \end{aligned}$$

Note that

$$\frac{\partial s}{\partial \psi} \dot{\psi} = -\vec{\nabla} \cdot \vec{j}_\psi \frac{\partial s}{\partial \psi} = -\vec{\nabla} \cdot \left(\frac{\partial s}{\partial \psi} \vec{j}_\psi \right) + \vec{\nabla} \frac{\partial s}{\partial \psi} \cdot \vec{j}_\psi$$

and

$$\vec{\nabla}\psi \cdot \dot{\vec{\nabla}}\psi = \vec{\nabla} \cdot (\dot{\psi} \vec{\nabla}\psi + \nabla^2\psi \vec{j}_\psi) - \vec{\nabla}(\nabla^2\psi) \cdot \vec{j}_\psi.$$

Moreover

$$\begin{aligned} \nabla^2\psi \nabla^2 \dot{\psi} &= \vec{\nabla} \cdot [\nabla^2\psi \vec{\nabla}\dot{\psi} - \dot{\psi} \vec{\nabla}(\nabla^2\psi) - \nabla^4\psi \vec{j}_\psi] \\ &\quad + \vec{\nabla}(\nabla^4\psi) \cdot \vec{j}_\psi. \end{aligned}$$

According to Eqs. (11), (12), and (13), we obtain

$$\begin{aligned} \vec{j}_S &= \frac{\partial s}{\partial \psi} \vec{j}_\psi + \alpha_2 (\dot{\psi} \vec{\nabla}\psi + \nabla^2\psi \vec{j}_\psi) \\ &\quad + \alpha_3 [\nabla^2\psi \vec{\nabla}\dot{\psi} - \dot{\psi} \vec{\nabla}(\nabla^2\psi) - \nabla^4\psi \vec{j}_\psi] \end{aligned} \quad (14)$$

and

$$\sigma_S = \vec{j}_\psi \cdot \left[\vec{\nabla} \left(\frac{\partial s}{\partial \psi} + \alpha_2 \nabla^2\psi - \alpha_3 \nabla^4\psi \right) - \alpha_1 \dot{\vec{j}}_\psi \right]. \quad (15)$$

Because σ_S is *non-negative*, we get

$$\vec{j}_\psi = M \left[\vec{\nabla} \left(\frac{\partial s}{\partial \psi} + \alpha_2 \nabla^2\psi - \alpha_3 \nabla^4\psi \right) - \alpha_1 \dot{\vec{j}}_\psi \right]. \quad (16)$$

Substituting \vec{j}_ψ in Eq. (8) we obtain

$$\alpha_1 M \frac{\partial^2 \psi}{\partial t^2} + \frac{\partial \psi}{\partial t} = \vec{\nabla} \cdot M \vec{\nabla} \left(\alpha_3 \nabla^4 \psi - \alpha_2 \nabla^2 \psi - \frac{\partial s}{\partial \psi} \right) \quad (17)$$

Recalling that

$$\frac{\partial s}{\partial \psi} = -\frac{1}{T} \frac{\partial f}{\partial \psi}, \quad (18)$$

and assuming that the mobility M is a constant, we have

$$\alpha_1 M \frac{\partial^2 \psi}{\partial t^2} + \frac{\partial \psi}{\partial t} = \frac{M}{T} \nabla^2 \left(\alpha_3 T \nabla^4 \psi - \alpha_2 T \nabla^2 \psi + \frac{\partial f}{\partial \psi} \right) \quad (19)$$

Eq. (19) is the central result of the paper. It is now straightforward to see that Eq. (19) is identical to the Modified Phase Field Crystal (MPFC) equation [18]. If $\alpha_1 = 0$, this equation reduces to the Phase Field Crystal (PFC) equation. If $\alpha_3 = 0$, it reduces to the Modified Cahn-Hilliard (MCH) equation [22]. Moreover, if $\alpha_1 = \alpha_3 = 0$, it reduces to the Cahn-Hilliard (CH) equation. Since α_1 , α_2 and α_3 are associated with the extended independent variables \vec{j}_ψ , $\vec{\nabla} \psi$ and $\nabla^2 \psi$, we see the importance of including those variables in Eq. (5) and how each variable plays a different role in obtaining the existing models.

By comparing Eq. 19 with Eq. 25 in Ref. 22, we find $\alpha_1 = \tau_D/M$, where τ_D is the relaxation time for the solute. τ_D can be considered as the time needed to smooth concentration inhomogeneities by diffusion. As to the other two parameters α_2 and α_3 , a comparison with Eq. 1 and Eq. 2 reveals that α_2 (related to the interfacial width) is positive when $\alpha_3 = 0$. When $\alpha_3 \neq 0$, α_2 has to be negative and α_3 has to be positive to form a periodic phase [14].

In summary, we have shown how the four models from Tab. I that have a conserved phase field variable, can be derived in a unified way by introducing two new extended independent variables in Eq. (5). This puts the MPFC model – which was originally based on a postulated equation of motion – on a more solid theoretical foundation. Our derivation implies a proof of thermodynamic consistency for all four models in a unified framework. Models with and without fast dynamics were treated on the same footing. As an outlook to further work, we suggest exploiting further the concept of thermodynamic consistency in the PFC case: derive sharp interface equations that correspond to the amplitude equations derived for PFC models [23, 24] for physically relevant problems, where a microscopic sharp interface model does not yet exist. As sharp interface models offer different possibilities for analytical treatment, they can contribute further to a more comprehensive understanding of the underlying physical system. In addition, the methodology presented in the paper could be potentially further applied

to find models for a broader range of physical systems, for example, the yet-to-be-developed Modified Swift Hohenberg (MSH) model in Tab. I, as the analysis for a non-conserved phase field variable can be done in a similar way, with flux being replaced by time derivative in the extended space Eq. (5).

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